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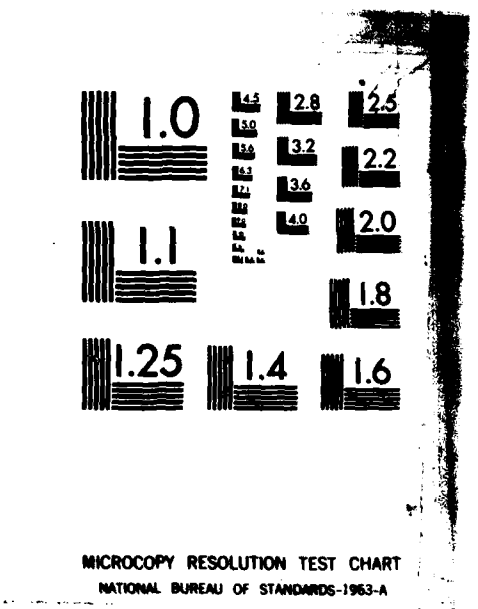

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EFFECT OF UV ILLUMINATION ON THE SUBLIMATION OF BASAL SURFACES OF ZINC OXIDE*

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Despite substantial agreement in the measured kinetics for the sublimation of basal surfaces of zinc oxide crystals, differing mechanisms have been proposed. To help resolve the questions, the effect of photoexcitation on the ZnO basal plane sublimation rate was studied. Single crystals were illuminated by ultraviolet irradiation of 0.177 mW/~~mm~~^{2}, or 4 photons/site-sec. Three wave lengths between 300-375 nm gave the same result, i.e., a small decrease in rate for the (0001) surface, and a small increase for the (000$\bar{1}$) surface. This result supports the model for surface charge effects resulting from oppositely (cont'd)

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Block 20 (Abstract) - Continued

charged surface kinks by Hirth et al, and opposes the model for rate control by charge recombination at surface sites by Hirschwald et al.

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EFFECT OF UV ILLUMINATION ON THE SUBLIMATION OF BASAL SURFACES OF ZINC OXIDE

by

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Introduction

The results of several studies on the sublimation rates of (0001) and (000$\bar{1}$) surfaces of zinc oxide crystals are in substantial agreement concerning the magnitudes of the sublimation coefficient α, 10^{-3} and 10^{-4}, respectively, as recently reviewed.[1,2] On the basis of the effect of oxygen and lithium doping on ZnO sublimation rates, McVicker et al[3] interpreted their measurements in terms of surface charge effects associated with opposite sign kinks on the surface. Hirschwald and coworkers,[4-6] rationalizing photolysis rates on ZnO at lower temperatures, interpreted their results in terms of a charge recombination rate-controlling step at surface sites, which could be kinks.

Specifically, McVicker et al[3] found that increased oxygen pressure reduced the rate of sublimation of ZnO (0001) surfaces at high temperatures, but increased the rate for (000$\bar{1}$) surfaces. They discussed the results in terms of an effective charge of 2 for both zinc and oxygen ions. Now, it appears that an effective charge of 1 is a better approximation,[1] so the modified surface--bulk equilibria in Kroger's notation[7] are

$$k_{Zn}^{\bullet/2} + O_O^x = V_O^{\bullet}(Z) + k_O^{'/2} + Zn_{Zn}^x \qquad (1)$$

or the equivalent with $Zn_i^{\bullet}(Z)$ as an alternate donor and

$$e'(Z) + \tfrac{1}{2} O_2\,(g) + k_{Zn}^{\bullet/2} = k_O^{'/2} + Zn_{Zn}^x \qquad (2)$$

Here $k_{Zn}^{\bullet/2}$ and $k_O^{'/2}$ are cation and anion kinks, respectively, which carry half-unit charges, $V_O^{\bullet}$ is an anion vacancy at a distance Z from the surface, e' is an electron and the sites with superscript x are normal lattice ions. An excess of cation or anion kinks produces a surface charge Q, positive or negative, respectively, which is hypothesized to influence the activation energy for sublimation.

Hirschwald et al[2,4-6] based their interpretation for the rate-limiting step in ZnO sublimation on the close agreement of the activation energy for sublimation and the room temperature band-gap energy[1-7] in zinc oxide of $\sim$ 3.2 eV. However, at a temperature of 1000°C, typical of the sublimation experiments, the band gap[1,7] is only 2.2 eV so the above correspondence is questionable.

In view of questions about the rate controlling mechanism of ZnO sublimation, experiments were undertaken to determine the effect of photoexcitation on the rate of sublimation. If charge recombination were rate controlling, the increased electronic charge carrier density produced by photoexcitation should increase the rate from both basal surfaces, while this need not be so for the other model.

Experiment

The apparatus used was that described by McVicker et al.[3] Briefly, a ZnO single crystal with one basal surface exposed was heated in high vacuum by focussed infra-red lamps and its weight loss was continuously monitored with a Cahn microbalance. The zinc oxide crystals, supplied by the 3M Company, were of comparable purity to the earlier work,[3] 30 ppm total impurities with Cu (8 ppm) and Si (5 ppm) the major ones. The main difference was that a Bausch and Lomb monochrometer was used to illuminate the subliming crystals. The ultraviolet irradiation of 0.177 mW/mm^2 is equivalent to a flux of 4 photons per surface ionic site per second. The wavelengths used, 300, 354, and 372 nm, gave identical results and were well below the minimum threshold as a function of temperature of 871 nm (corresponding to the maximum band gap energy) needed for photoexcitation.

Weight loss rates were reproducible within 2 %. Through the relation

$$ZnO(s) = Zn(g) + \tfrac{1}{2} O_2(g) \qquad (3)$$

the weight losses were converted to sublimation fluxes of Zn and O_2. Through the Hertz-Knudsen relation, these fluxes were converted to effective pressures p^*_{Zn} and $p^*_{O_2}$ and thence to an effective coefficient $p^*_{Zn}\, p^{*\,1/2}_{O_2}$. This coefficient has the same form as the equilibrium constant for Eq. (3) and can be used to determine an activation enthalpy to compare to the equilibrium value.

Results and Discussion

As shown in Fig. 1, the results agree well with the earlier work in the absence of irradiation. Activation enthalpies determined from the relation

$$\Delta H^* = -R\partial \ln [P^*_{Zn}(P^*_{O_2})^{1/2}]/\partial(1/T) \qquad (4)$$

i.e., from the temperature dependence of the effective equilibrium constant of Eq. (3), were 519 ± 17 kJ/mol (0001) and 565 ± 15 kJ/mol (000$\bar{1}$) compared to the earlier results[3] of 520 ± 14 kJ/mol and 566 ± 11 kJ/mol, respectively. Values for ΔS were 200 J/K mol (0001) and 215 J/K mol (000$\bar{1}$) compared to earlier results[3] of 194 J/K mol and 213 J/K mol, respectively.

The effect of illumination is shown in Fig. 2, producing a decrease in rate of 5.5 ± 0.75 percent for the (0001) surface and an increase of 3.5 ± 1.3 percent for the (000$\bar{1}$) surface. If the effect were instead one of enhanced recombination, one would expect an increase for both surfaces, so the results support the model of sublimation controlled by Q. Of significance, the direction of the effect produced by photoexcitation is the same as that produced by increased oxygen pressure. Both effects would be consistent with a positive surface charge Q for the (000$\bar{1}$) surface with either increased p_{O_2} or increased electron concentration shifting the equilibrium of Eq. (2) to the right, decreasing Q and thereby decreasing ΔH^* and increasing the rate. This is similar to the explanation of photolysis by Hirschwald et al[1,2,5,6] but relates the effect to Q, i.e. to the relative kink concentrations, rather than to the total numbers of surface species (holes and kinks). The effects would be consistent with a negative surface charge on the (0001) surface (contrary to the earlier interpretation[3]) with a shift of Eqs. (1) and (2) to the right decreasing the rate.

Acknowledgment

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Figure Captions

Fig. 1. Least squares fit of experimental data for zinc oxide sublimation, (solid circles and squares) of McVicker et al[3], solid line, together with current results (open circles and squares). The dashed line denotes equilibrium.

Fig. 2. Least squares fit of current results from Fig. 1, open triangles and circles and solid lines, together with the results under illumination, solid triangles and circles and dashed lines.

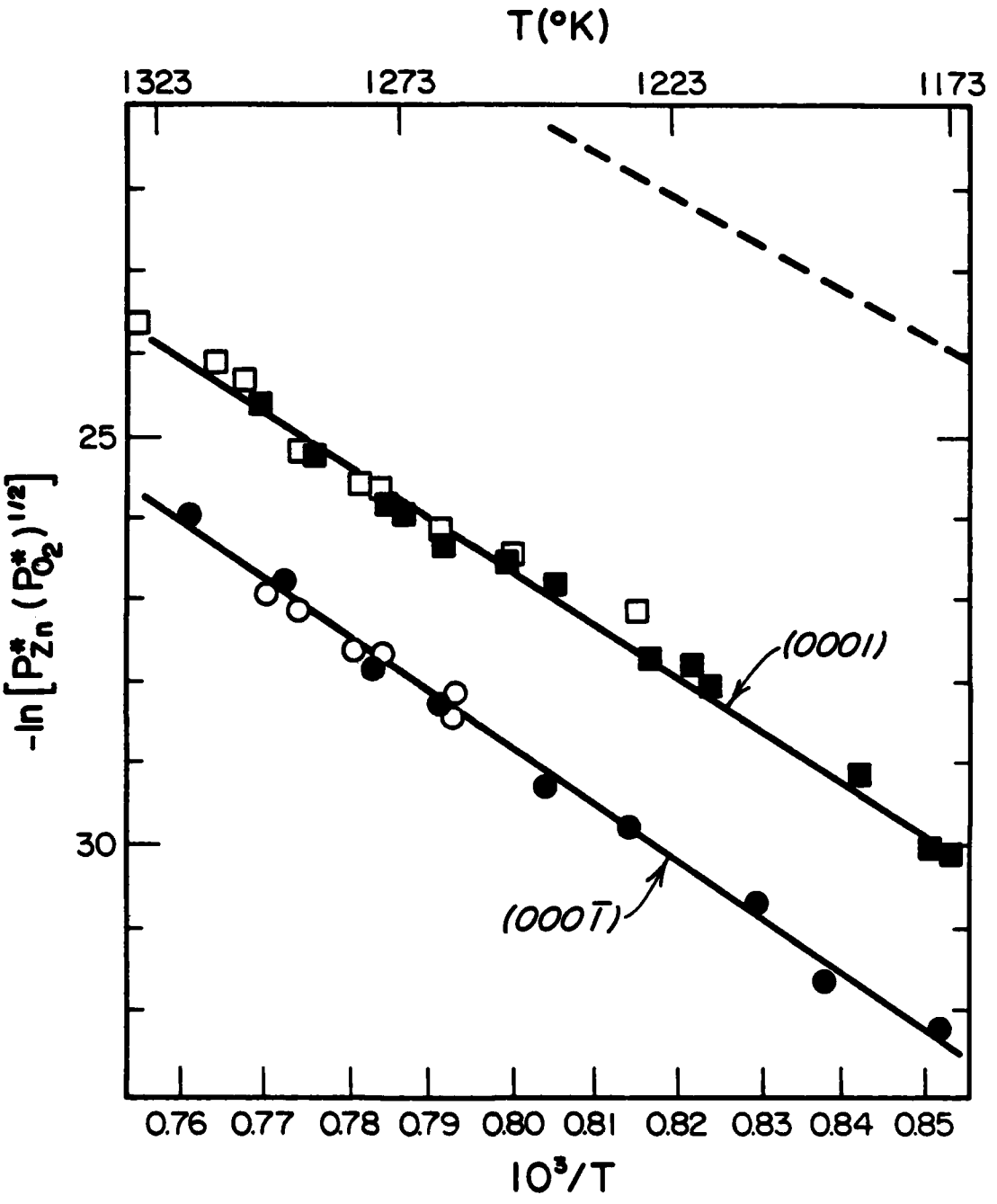
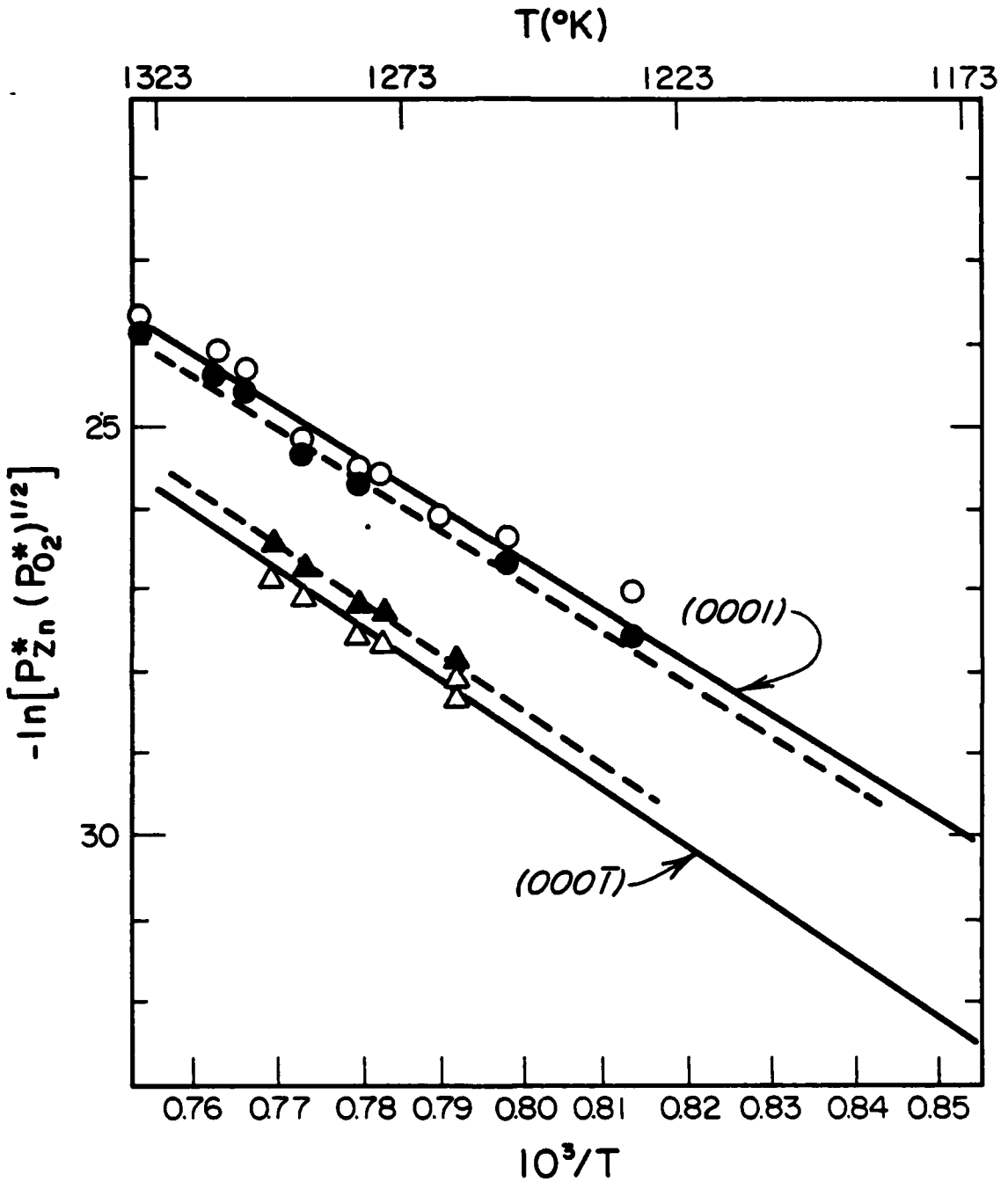


Fig 1 Carey et al



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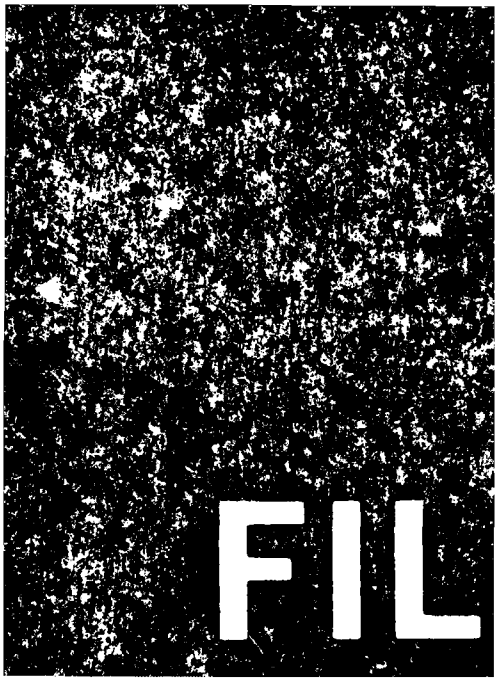
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